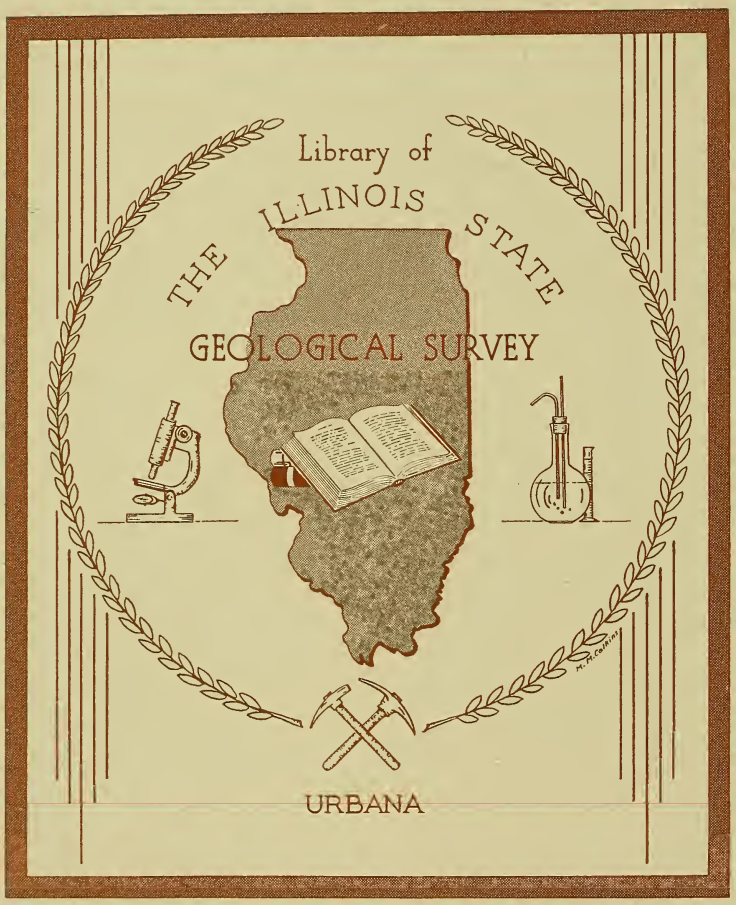
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METHODS FOR DETERMINING FLUORINE

BY

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Methods for Determining Fluorine*

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Fluorine ranks nineteenth in the order of abundance of the elements in the earth's crust, being three times as abundant as copper and fifteen times as abundant as lead. But in spite of its abundance, the chemistry of fluorine and its compounds is the least understood of the common elements. The reason is due in part to the extreme reactivity, the toxicity, and to the large number of anomalies occurring in fluorine and its compounds.

Fluorides are met with in (1) drinking water where "fluorosis" or mottled teeth may be produced, (2) the removal of fluorine from phosphate fertilizer made from fluorapatite, (3) the increasing use of fluorides as fungicides and insecticides, (4) organic fluorides used in electrical refrigeration, the dyeing of fabrics, electrical transformer oils, and various solvents.

To analyze a fluoride it is first necessary to convert it to a soluble fluoride, most always sodium fluoride. With inorganic fluorides decomposition can be effected by sintering with calcium oxide in a closed nickel tube or by ignition with sodium peroxide, sugar and potassium chlorate in a Parr bomb. By far the most applicable method is fusion with sodium and potassium carbondates with a tenfold excess of silica flour. This converts the fluorine to soluble alkali fluoride and all cations to insoluble silicates, thus effecting an easy separation of most interfering substances.

Organic fluorides must first be decomposed and converted into inorganic. A convenient means of effecting decomposition is by ignition with oxygen in a silica tube, packed with crushed silica and maintained at a temperature of 900° C. To utilize this method, the organic fluoride must be capable of being brought to the vapor state. Decomposition is rapid and complete, the fluorine being volatilized as silicon tetrafluoride which is absorbed in a solution of sodium hydroxide. This appears to be the best method available for gaseous fluorides. Another method applicable to organic fluorides, except for gaseous fluorides, is decomposition with metallic sodium in liquid ammonia. The organic fluoride is dissolved in liquid ammonia, with the aid of a suitable solvent inert to sodium such as ether, tributylamine, etc. Small pieces of sodium are slowly introduced until an excess is indicated by the blue color of ionized sodium. The excess sodium is then destroyed with ammonium nitrate or by the cautious addition of water. The fluorine of the organic fluoride is then in solution as sodium fluoride. Organic fluorides can also be decomposed by ignition with calcium oxide or in a Parr bomb with sodium peroxide and potassium chlorate. The last two methods cannot always be relied upon for quantitative decomposition.

When the fluoride being analyzed has been converted to soluble sodium fluoride all interfering substances must be removed. The old Berzelius method involving the precipitation of the cations gives low results due to adsorption. The best method to date is the distillation method of Willard and Winters. An ordinary 250 cc. distillation flask equipped with a special spray trap and connected to an ordinary Liebig condenser is used. A piece of glass tubing extends to the bottom of the flask through which steam can

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be blown. A thermometer also extends to the bottom of the flask. To distil, the impure fluoride is introduced into the flask together with 20 cc. of concentrated sulfuric or perchloric acid. The liquid in the flask is maintained at a temperature of 135° C. and steam distilled so that the distillate comes over at a rate not exceeding 90 cc. per hour. Ordinarily 150 cc. of distillate is sufficient to contain all of the fluorine.

In all gravimetric methods the silica must be removed by evaporation to near dryness with ammonium hydroxide and the silica filtered off. Such a procedure always leaves an appreciable quantity of silica which must be taken out with ammoniacal zinc oxide. After the removal of silica, the fluoride ion can be precipitated in acetic acid solution with calcium or lanthanum nitrate thus precipitating calcium or lanthanum fluoride which is filtered, washed, ignited, and weighed. Fluoride ion can also be precipitated with lead chloride as the lead chlorofluoride salt. The chief difficulties of the latter three methods are the slimy nature and appreciable solubility of the precipitates. A relatively new procedure uses triphenyl tin chloride as the precipitating agent which precipitates the fluorine as the extremely insoluble and crystalline triphenyl tin fluoride. Due to the low solubility of the precipitating agent not more than forty milligrams of fluorine can be conveniently handled.

The fluoride ion can be accurately determined colorimetrically if close attention is given to all details such as volume, temperature, acidity, etc. The Steiger-Merwin method depends upon the fact that the fluoride ion bleaches the yellow color produced on treating titanium salt with hydrogen peroxide. Standards are made up with known amounts of fluoride ion and compared with the unknown in ordinary Nessler tubes. This method fails with over two per cent of fluorine.

The De Boer method depends upon the fact that fluoride ion bleaches the pink color of a solution of zirconium nitrate and sodium alizarin sulfonate and is carried out in the same manner as the Steiger-Merwin method.

The conductometric methods are the least satisfactory of all due to the unstable and widely varying end points.

The volumetric methods, in general, give the most reliable results in determining the fluoride ion. Titration with ferric chloride using ammonium thiocyanate as indicator is useful when the concentration of fluoride is large. The titration is carried to the appearance of the pink color of ferric thiocyanate, ferric fluoride being un-ionized fails to react with ammonium thiocyanate.

An indirect method for the determination of fluorine involves the precipitation of the fluoride ion as cerous fluoride with excess cerous nitrate. The excess cerous nitrate is determined by titration with potassium permanganate, which furnishes its own indicator. Due to the hydrolysis of ceric nitrate to form nitric acid, the titration must be done in the presence of an excess of zinc oxide.

Probably the most accurate volumetric method is by titration with thorium nitrate using a buffer, proposed by Ferris and Hoskins of trichloroacetic acid, with a zirconyl chloride-sodium alizarin sulfonate indicator. The amount of fluorine must be small, not over twenty milligrams and the thorium nitrate solution should not be stronger than 0.017 N.

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